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Processes of microbial pesticide degradation in rapid sand filters for treatment of drinking water

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Abstract: Aerobic rapid sand filters for treatment of groundwater at waterworks were investigated for the ability to remove pesticides. The potential, kinetics and mechanisms of microbial pesticide removal was investigated in microcosms consisting of filter sand, treated water and pesticides in initial concentrations of 0.04-2.4 µg/L. The pesticides were removed from the water in microcosms with filter sand from all three investigated sand filters. Within the experimental periode of six to 13 days, 65-85% of the bentazone, 86-93% of the glyphosate, 97-99% of the *p*-nitrophenol was removed from the water phase. Investigations of the removal kinetics of bentazone at Sjælsø waterworks Plant II revealed that more than 50% of bentazone was removed within 30 minutes (initial concentrations 0.1-2.4 µg/L). Ammonium and methane is oxidized by bacteria in rapid sand filters, and these are known to degrade xenobiotics by cometabolic processes. It was investigated if addition of ammonium affected bentazone removal or if removal was affected by addition of allylthiourea, which inhibits ammonium oxidizing bacteria. Preliminary results indicated that addition of ammonium as well as allylthiourea affected the removal of bentazone.

Keywords: pesticides, microbial degradation, rapid sand filtration, potential, kinetics, processes

Introduction

Groundwater is a widespread drinking water source in Europe where 70% of the population is supplied by treated groundwater (Navarrete et al., 2008). Unfortunately, large parts of this groundwater are contaminated by pesticides and in the European Union (EU) the concentration of pesticides in drinking water and groundwater should not exceed 0.1 µg/L for a single compound (European Parliament and Council, 2000). In Denmark approx. 100% of the drinking water is treated groundwater, and in the period from 2010-2012 pesticides were detected in 20-25% of the active waterworks wells (Figure 1) (GEUS, 2013). Pesticides can be removed from the water phase by advanced treatment methods such as granular activated carbon (GAC) (e.g. Heijman et al., 2002) and advanced oxidation processes (e.g. Suty et al., 2004). In Denmark, waterworks are not designed to remove pesticides and treatment consists of aeration followed by filtration in primary and secondary rapid sand filters. Therefore common practice is to substitute contaminated wells. However, recent investigations have shown potential for removal of the pesticide MCPP in full-scale rapid sand filters at a groundwater-based waterworks (Corfitzen et al., 2009) others have found that biological filters used to treat surface water are able to remove pesticides after a six-month adaption period (Zearley and Summers, 2012) and Hedegaard and Albrechtsen (2014) found a potential for microbial removal of several pesticides in different rapid sand filters. A range of other compounds (e.g. ammonium and methane) are routinely oxidized in the rapid sand filters, and ammonium and methane oxidizing bacteria are known to be able to perform cometabolic degradation (Nazaroff and Alvarez-Cohen, 2001; Dalton and Stirling, 1982). Such organisms may be involved in the transformation of pesticides.

This study aims to investigate the potential, kinetics and mechanisms of microbial pesticide removal in rapid sand filters for drinking water treatment.

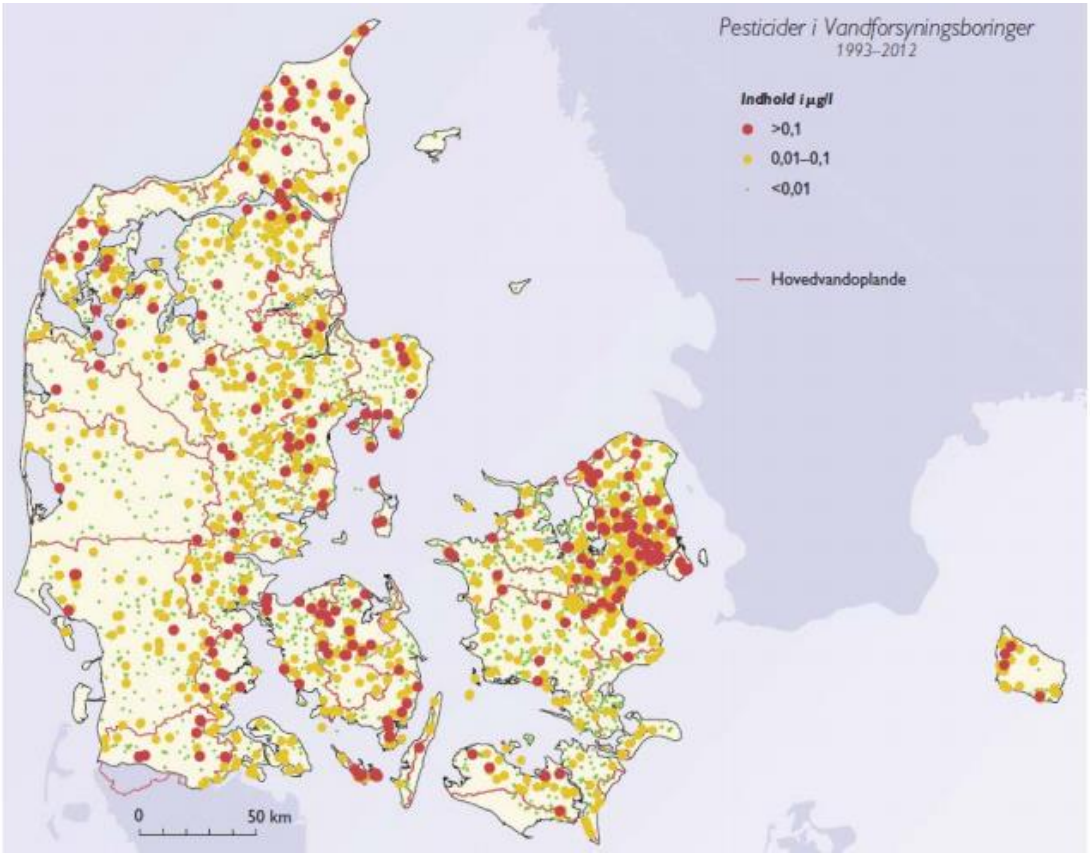

Figure 1 Detected pesticides in waterworks abstraction wells in Denmark during the period 1993-2012. Red dots marks wells with concentrations above the guideline value >0.1 µg/L, yellow dots with 0.01-0.1 µg/L and green dots <0.01 µg/L (GEUS, 2013).

Material and Methods

Filter sand was collected from the top 20 cm of the investigated rapid sand filter at Islevbro waterworks and Sjælsø waterworks Plant I and Plant II, and experiments were started within 24 hours after sampling. Microcosms were set-up with sand, water and initial pesticide concentrations of 0.04-2.4 µg/L (Figure 2). Water samples were collected from the microcosms. The pesticides were ^{14}C-labelled and the analysis was based on a double vial system where produced $^{14}CO_2$ from mineralisation of the pesticide was stripped off the water sample and captured by a base trap (1 mL 2M NaOH). Thus the produced $^{14}CO_2$ and the ^{14}C-activity of the pesticide in the water phase could be quantified (Figure 3).

To investigate how ammonium influenced the removal of pesticides, ammonium was added to microcosms in different concentrations (0; 0.9; and 4.8 mgN/L). Additionally, allylthiourea was added to inhibit ammonium oxidizing bacteria (in concentrations of 0.2 mg/L and 3.0 mg/L) in selected microcosms, to investigate if an inhibition of ammonium oxidation influenced the removal process.

Figure 2 Filter sand was collected from the top 20 cm of the rapid sand filters. Microcosms were constructed by adding filter sand, water and ^{14}C-labelled pesticide to serum bottles. **Top left**: Model of the rapid sand filter construction (filter depth 80 cm). **Bottom left**: Collection of filter sand. **Top right**: Filter sand addition to microcosms. **Bottom right**: Microcosms with sand, water and ^{14}C-pesticide.

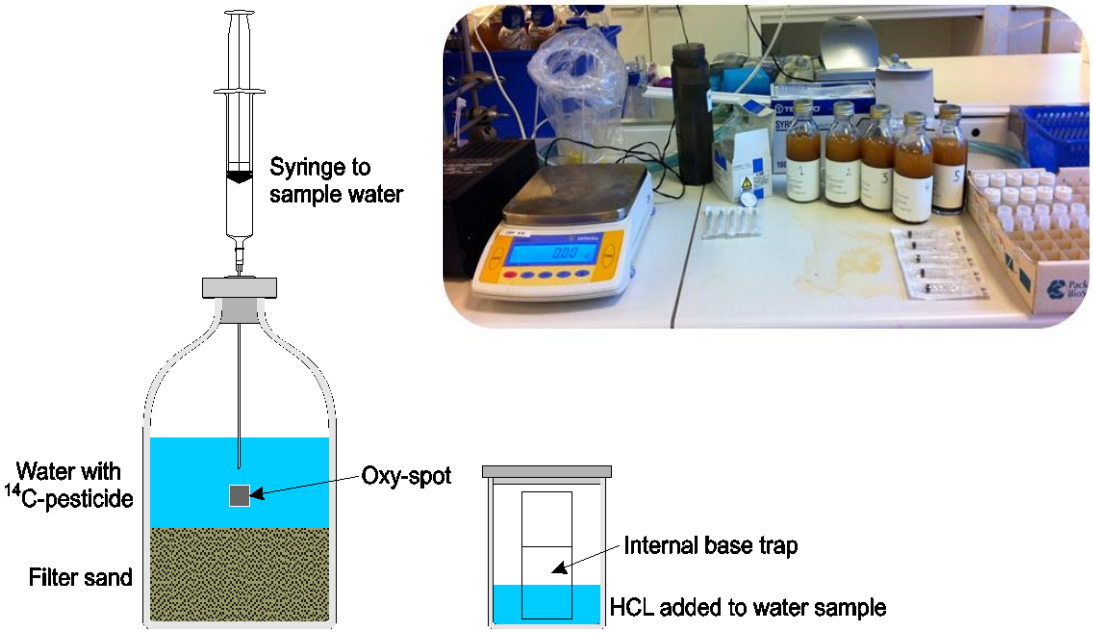

Figure 3 Microcosms consisting of filter sand, water and ^{14}C-pesticide. Water samples were collected, filtered and transferred to 20mL plastic vials. HCl was added to water samples to strip off $^{14}CO_2$ from mineralisation of ^{14}C-pesticide and $^{14}CO_2$ was caught by a base trap.

Results and Conclusions

At all three investigated rapid sand filters the added pesticides were removed from the water phase. During the experimental period of six to 13 days 65-85% of the initially added bentazone, 86-93% of the glyphosate and 97-99% of the *p*-nitrophenol was removed from the water phase (Figure 4).

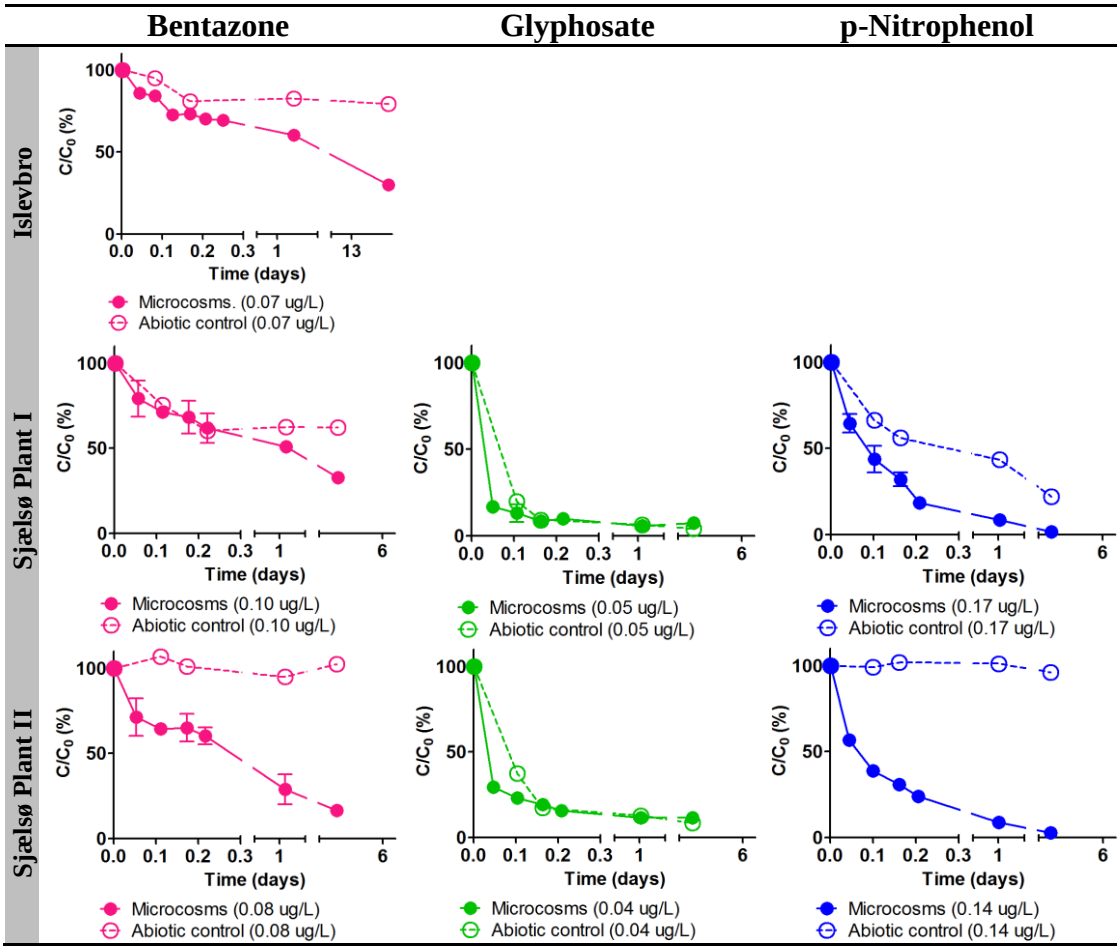

Figure 4 Potential for degradation of bentazone (pink), glyphosate (green) and *p*-nitrophenol (blue) with filter sand from Islevbro waterworks and Sjælsø water works Plant I and II, Denmark. The fraction of ^{14}C in the water phase of the initial amount of $^{14}C_0$ in the microcosms (duplicates) and abiotic controls (the initial concentrations are given in parenthesis).

More bentzone and *p*-nitrophenol was removed in the microcosms compared to the corresponding abiotic controls, demonstrating the removal in the microcosms was partial biological. This was not as evident for the removal of glyphosate, where removal in microcosms and abiotic controls were the same (Figure 4). However, the microbial degradation in the filter sand from Sjælsø waterworks Plant II led to a partial mineralisation of the pesticides – $^{14}CO_2$ production from bentazone reached 8-14%, glyphosate 42–43% and *p*-nitrophenol 7-10% of the initially added pesticide after 6 days (Table 1). Thus, all three pesticides were biologically degraded in filter sand from Sjælsø waterworks Plant II.

Bentazone is still legally used in the European Union (EU pesticide database, 2013) and has previously been found to be difficult to degrade in aquifers (Albrechtsen et al., 2001; Broholm et al., 2001). Therefore the biological removal of

bentazone at Sjælsø waterworks Plant II, was of particular interest and the removal kinetics of bentazone was investigate with filter sand from this filter, which had an contact time of 56 minutes.

Table 1. Fractionation of **^{14}C**-bentazone after incubation with filter material. The fraction of $^{14}CO_2$ of the initial amount of $^{14}C_0$ is shown after 6 days. Data are from microcosms (two replicates) and abiotic controls (Modified from Hedegaard and Albrechtsen, 2014).

	$^{14}CO_2$-production from degradation ($^{14}CO_2/^{14}C_0$)	
	Microcosms	**Abiotic control**
Sjælsø Plant II	**6 days**	
Bentazone	8-14%	B.D.
Glyphosate	42-43%	B.D.
4-nitrophenol	7-10%	B.D.

B.D. – Below detection limit

At Sjælsø waterworks Plant II the bentazone removal was initiated immediately when the experiment started and no adaptation period was observed. This is in contrast to degradation studies of bentazone with groundwater where bentazone removal was only initiated after a long adaptation phase (184 days) (Levi et al., 2014). Additionally, bentazone was removed very rapidly in the filter sand and in less than 30 minutes more than 50% of the bentazone was biologically removed at all tested initial concentrations 0.1-2.4 µg/L (Figure 5). This study is therefore important, since it for the first time demonstrates a very rapid microbial degradation of bentazone within the contact time of a rapid sand filter.

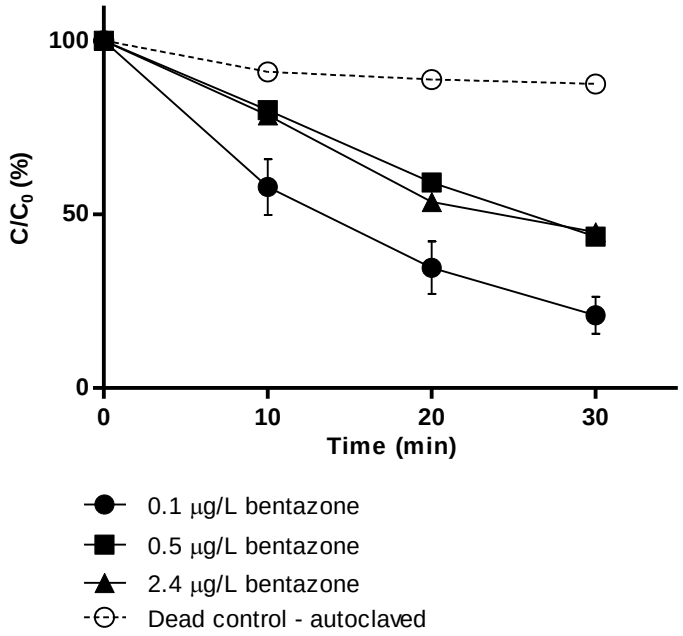

Figure 5 Sjælsø water works Plant II - Removal kinetics investigated at three different initial concentrations in a short term investigation. The mean concentrations and standard deviation are given as per cent of the initial concentration. Microcosms with initial concentration of 0.1 µg/L (triplicate) and corresponding abiotic control (initial concentration 0.1 µg/L) and two microcosms with initial concentrations of 0.5 µg/L and 2.4 µg/L (Modified from Hedegaard and Albrechtsen, 2014).

It was investigated how the bentazone removal was affected when ammonium was added and when ammonium oxidizing bacteria was inhibited by allylthiourea.

Preliminary results indicated that addition of ammonium decreased the removal of bentazone in the initial phase of the experiment: addition of ammonium to the microcosms in high concentrations (4.8 mg/L) resulted in removal of 54% of the bentazone after three hours, but 75% was removed when ammonium was not added. When allylthiourea was added to inhibit the ammonium oxidation, the removal of bentazone increased in microcosms with high ammonium concentrations in the initial phase of the experiment. Thus 56% of the bentazone was removed after six hours in the microcosms, while 78% was removed in the microcosm where allylthiouea was added. These results may indicate a relation between the enzymes conducting the ammonium oxidation (e.g. ammonium oxidase) and the removal of bentazone – and thus a co-metabolic process. However, the oxygen concentration decreased to very low concentrations in the microcosms during this experiment, and since ammonium oxidation consumes oxygen, increased addition of ammonium may lead to increased oxygen consumption, inhibiting the degradation of bentazone whereas addition of allylthiourea to inhibit the ammonium oxidation also may reduce the oxygen consumption. The interaction with oxygen concentration is important since the removal of bentazone depends very much on the presence of oxygen (Knauber et al., 2000; Hedegaard and Albrechtsen, 2014).

Subsequently, a similar experiment was conducted with constantly high oxygen concentrations and continuously monitoring to prevent that lack of oxygen availability limited the removal of bentazone. In this experiment there was no influence of adding ammonium to the microcosms but when allylthiourea was added to the microcosms the removal of bentazone decreased in the initial phase of the experiment. An interpretation of this could be that addition of ammonium did not affect the removal of bentazone since the enzymatic activity was high enough to degrade bentazone by cometabolic processes in presence of even increased concentration of the primary substrate (ammonium), but when allylthiourea was added to inhibit the ammonium oxidizing bacteria, the removal of bentazone decreased. However, allylthiourea is also known to inhibit other bacteria such as methanotrophs. Consequently, the interaction between bentazone removal the ammonium and methane oxidizing bacteria is still unresolved.

Conclusions

1. An evident removal potential of bentazone, glyphosate, and *p*-nitrophenol was shown in samples from rapid sand filters at three Danish waterworks. The microbial removal was largest in filter sand taken from Sjælsø Plant II
2. In filter sand from Sjælsø waterworks Plant II bentazone concentration in the water phase decreased to less than 50% of the initial concentration within 30 minutes at all investigated concentration (0.1-2.4 µg/L) as a result of microbial removal
3. It was investigated whether the removal of bentazone in the filter sand is a cometabolic degradation performed by ammonium oxidizing bacteria. However, the interaction between bentazone removal the ammonium and methane oxidizing bacteria is still unresolved.

This study showed that substantial microbial pesticide removal is possible within the contact time of rapid sand filters and thereby a potential for treatment of pesticide contaminated groundwater in Danish waterworks. This is of commercial interest due to the economical and environmental sustainability of this water treatment method.

Acknowledgements

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